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⑦① Applicant: **TORAY SILICONE COMPANY,
LIMITED**
2-3-16, Muro-machi Nihonbashi
Chuo-ku Tokyo 103(JP)

⑦② Inventor: Nakaya, Tadao
2-29, 4-chome Kitakasugaoka
Ibaraki-shi Osaka Prefecture(JP)
Inventor: Imoto, Minoru
46, 3-chome Okaminami-machi
Hirakata-Shi Osaka Prefecture(JP)

⑦④ Representative: Spott, Gottfried, Dr. et al
Patentanwälte Spott und Puschmann
Sendlinger-Tor-Platz 11
D-8000 München 2(DE)

⑤④ Organopolysiloxanes containing a phospholipid-like structure and a process for their preparation.

⑤⑦ The present invention provides linear and cyclic alkylpolysiloxanes and alkylhydrogenpolysiloxanes in which a functional group having a phospholipid-like structure (a trialkylammoniumphosphatidylalkyl group) and an alkyl group are bonded to the same silicon atom.

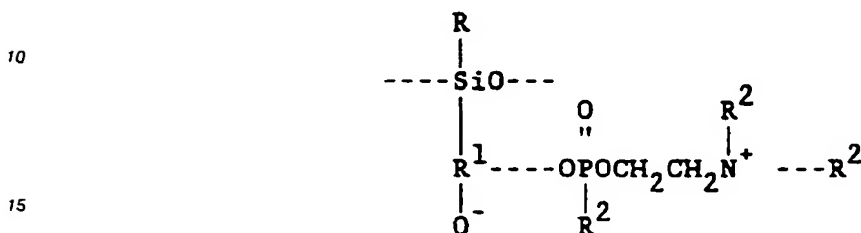
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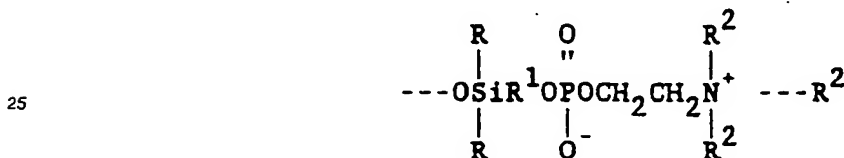
ORGANOPOLYSILOXANES CONTAINING A PHOSPHOLIPID-LIKE STRUCTURE AND A PROCESS FOR THEIR PREPARATION

The present invention relates to organopolysiloxanes which contain a phospholipid-like structure, and to a process for their preparation.

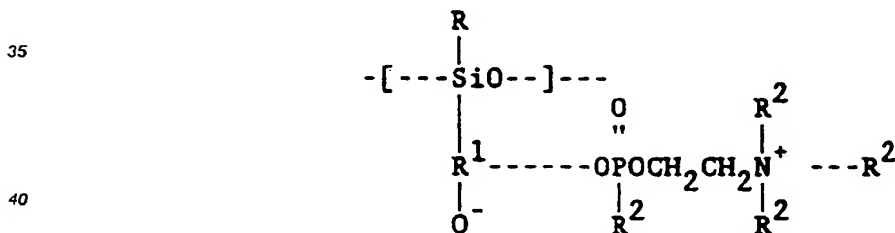
Organopolysiloxanes containing various functional groups and processes for their preparation are known in the prior art. These methods generally consist of contacting an unsaturated organic compound containing a functional group such as polyoxyalkylene oxide, cyano, acetoxy groups, or the like, with an organohydrogenpolysiloxane, under the influence of a hydrosilylation catalyst. However, unknown to the art are organopolysiloxanes containing a phospholipid-like structure having the unit formula



wherein each R is an alkyl radical, each R¹ is an alkylene radical containing 3 to 50 carbon atoms, and each R² is independently selected from the hydrogen atom, alkyl radicals containing 1 to 25 carbon atoms, and a siloxane with the unit formula

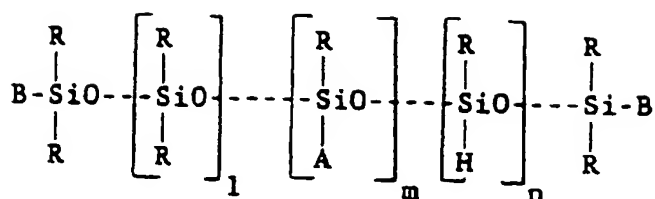


wherein R, R¹, and R² are defined above, and which may contain at least 1 of any of the following: a dialkylsiloxane unit, an alkylhydrogensiloxane unit, a trialkylsiloxy unit, and a dialkylhydrogensiloxy unit. Also unknown to the art are cyclic organopolysiloxanes containing a phospholipid-like structure, having the unit formula:

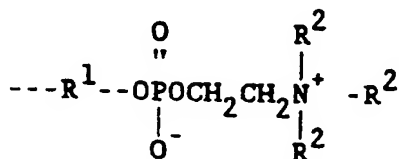


wherein R, R¹, and R² are defined above, and which may contain the dialkylsiloxane unit and/or alkylhydrogensiloxane unit.

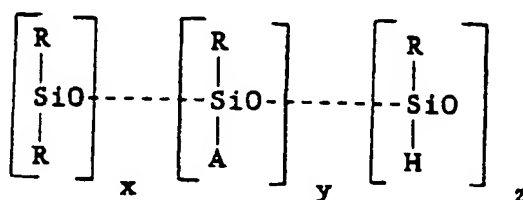
One element of the present invention relates to linear organopolysiloxanes containing a phospholipid-like structure, characterized in that they have the following general formula which has at least one group A in each molecule



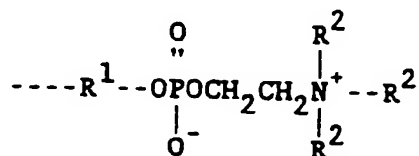
wherein R is an alkyl radical; A is an organic group having the unit formula



wherein R¹ is an alkylene group containing 3 to 50 carbon atoms and each R² is selected from hydrogen atoms or alkyl groups containing 1 to 25 carbon atoms; B is a group R, the hydrogen atom, or a group A; 1, m, and n, each have a value of zero or an integer of at least 1, with the proviso that 1 + m + n is an integer having a value of 0 to 2,000. A second element of the invention relates to cyclic organopolysiloxanes containing a phospholipid-like structure, characterized in that it has the general formula

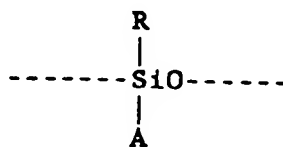


wherein R is an alkyl group, A is an organic group with the unit formula:

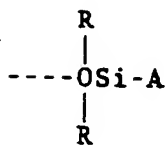


wherein R¹ is an alkylene group containing 3 to 50 carbon atoms and each R² is selected from hydrogen atoms or alkyl groups containing 1 to 25 carbon atoms, x is zero or an integer having a value of at least one, y is an integer having a value of at least one, and z is zero or an integer having a value of at least one, with the proviso that x + y + z is an integer having a value of 3 to 20.

The organopolysiloxanes having the general formula (I) are linear, and contain in the main chain the siloxane unit with the formula



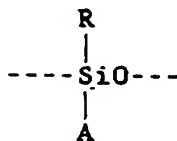
wherein R and A are defined above, and are endblocked by a siloxane unit with the formula



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They can also contain the dialkylsiloxane unit or alkylhydrogensiloxane unit or both such siloxane units in the main chain.

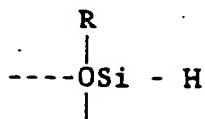
10 When the siloxane unit with the formula



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is present in the main chain, the molecular terminal may be a siloxane unit with the formula

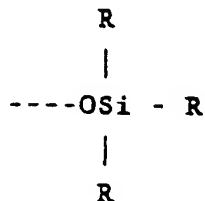
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or a siloxane unit with the formula

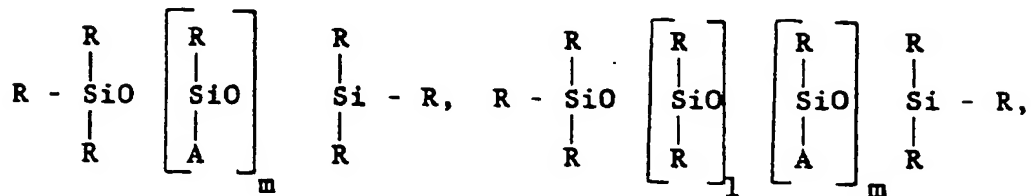
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Typical examples of organopolysiloxane with general formula (I) include

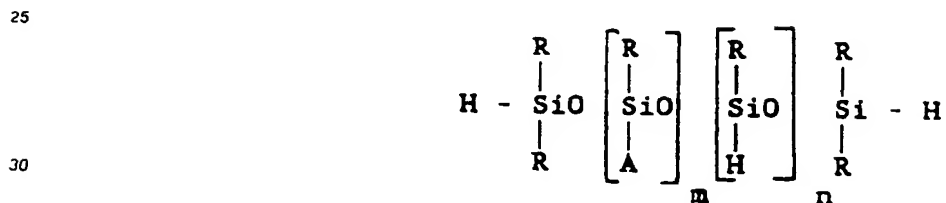
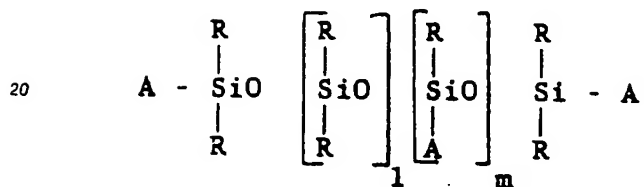
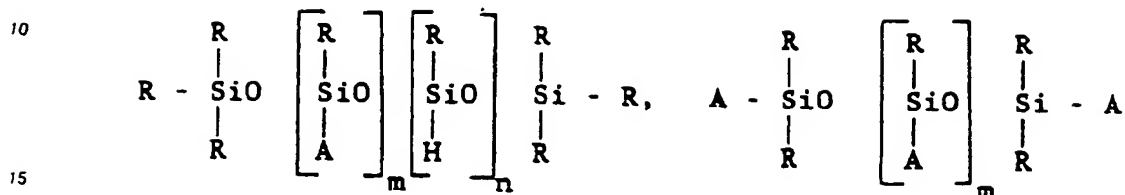
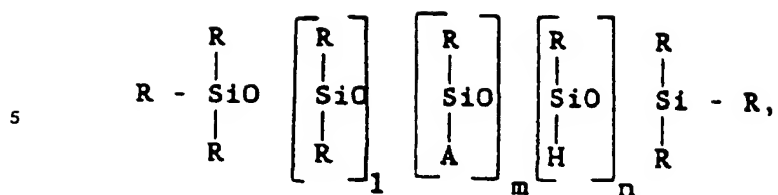
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When the dialkylsiloxane unit or alkylhydrogensiloxane unit or both types of siloxane units are present, along with the siloxane unit with the formula



these siloxane units are generally randomly arranged. In the general formula (I), l, m, and n are each zero or an integer with a value of at least 1, with the proviso that 1 + m + n is an integer with a value of 0 to 2,000. Thus, neither l nor m nor n can exceed 2,000. This upper limit of 2,000 on l + m + n is based on limitations on the technology for the synthesis of the precursor alkylhydrogenpolysiloxane starting material for organopolysiloxane with general formula (I).

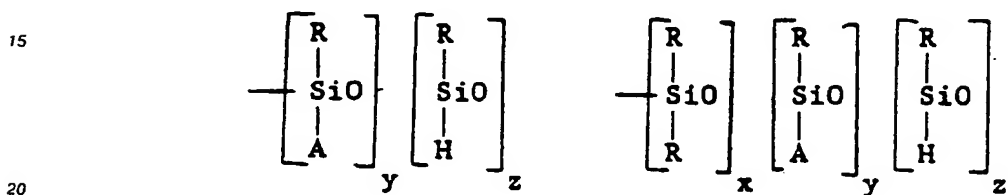
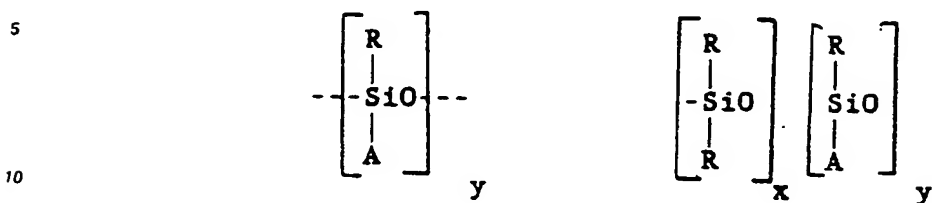
The organopolysiloxanes with the general formula (II) are cyclic, and contain at least one siloxane unit with the formula



and can additionally contain the dialkylsiloxane unit, or the alkylhydrogensiloxane unit, or both the

dialkylsiloxane unit and alkylhydrogensiloxane unit.

Typical examples of organopolysiloxane with the general formula (II) include the following:



When the dialkylsiloxane unit, alkylhydrogensiloxane unit, or both types of siloxane units are present along with the siloxane unit with the formula:



these siloxane units are generally randomly arranged.

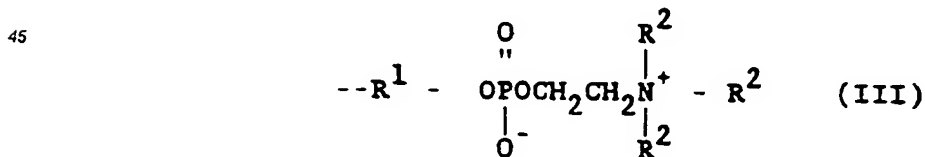
In general formula (II), x is zero or an integer with a value of at least 1, y is an integer with a value of at least one, and z is zero or an integer with a value of at least 1, with the proviso that x + y + z is an integer with a value of 3 to 20.

Thus, x will not exceed 19, y will not exceed 20, and z will not exceed 19.

The upper limit of 20 on x + y + z is based on limitations on the technology for the synthesis of the cyclic alkylhydrogenpolysiloxane starting material for organopolysiloxanes with the general formula (II).

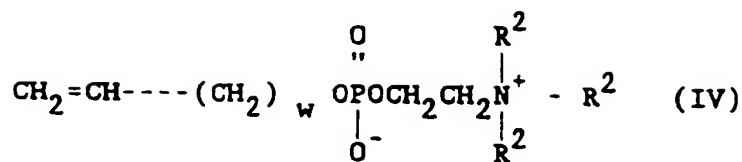
With regard to general formulas (I) and (II), R is an alkyl group, and is exemplified by methyl, ethyl, propyl, butyl, hexyl, octyl, and dodecyl. The groups R can be a mixture of different types within a single molecule. R is preferably the methyl group.

The group A is an organic group containing a phospholipid-like structure, and has the following formula.



Wherein R¹ is an alkylene group having 3 to 50 carbon atoms, and examples of this alkylene group are propylene, butylene, hexylene, octylene, and dodecylene. The group R² is the hydrogen atom or an alkyl group having 1 to 25 carbon atoms, and the alkyl group in this case is exemplified as for the group R. It is not necessary that the three groups R bonded to nitrogen be identical.

The linear organopolysiloxane with general formula (I) can be produced by a hydrosilylation reaction, in the presence of a hydrosilylation catalyst, between a compound having the formula:



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wherein w is an integer with a value of 1 to 48 and R^2 is defined as above and a trialkylsiloxy-terminated or dialkylhydrogensiloxy-terminated alkylhydrogenpolysiloxane, or a trialkylsiloxy-terminated or dialkylhydrogensiloxy-terminated dialkylsiloxane-alkylhydrogensiloxane copolymer.

10 Cyclic organopolysiloxane with general formula (I) can be produced by a hydrosilylation reaction, in the presence of a hydrosilylation catalyst, between a cyclic alkylhydrogenpolysiloxane or cyclic dialkylsiloxane-alkylhydrogensiloxane copolymer and a formula (IV) compound.

At this point, when the number of equivalents of vinyl groups in the formula (IV) compound is equal to or exceeds the number of equivalents of hydrosilyl groups in the alkylhydrogenpolysiloxane or dialkylsiloxane-alkylhydrogen siloxane copolymer, one obtains organopolysiloxane with general formula (I) in which n is zero and the group B is not a hydrogen atom, or organopolysiloxane with general formula (II) in which z is zero, that is, organopolysiloxanes lacking the alkylhydrogensiloxane unit.

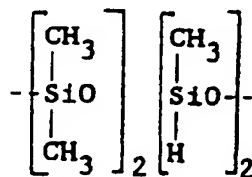
On the other hand, when the number of equivalents of vinyl groups in the formula (IV) compound is less than the number of equivalents of hydrosilyl groups in the alkylhydrogenpolysiloxane or dialkylsiloxane-alkylhydrogensiloxane copolymer, one obtains organopolysiloxane with general formula (I) in which n is at least 1 and/or B is a hydrogen atom, or organopolysiloxane with general formula (II) in which z is at least 1, that is, organopolysiloxane containing the alkylhydrogensiloxane unit.

Typical examples of the trialkylsiloxy-terminated or dialkylhydrogensiloxy-terminated alkylhydrogenpolysiloxane starting material for the linear organopolysiloxane with general formula (I) include trimethylsiloxy-terminated and dimethylhydrogensiloxy-terminated methylhydrogenpolysiloxanes.

Typical examples of the trialkylsiloxy-terminated or dialkylhydrogensiloxy-terminated dialkylsiloxane-alkylhydrogensiloxane copolymers include trimethylsiloxy-terminated and dimethylhydrogensiloxy-terminated dimethylsiloxane-methylhydrogensiloxane copolymers.

30 Tetramethyltetrahydrogencyclotetrasiloxane is a typical example of the cyclic alkylhydrogenpolysiloxane starting material for the cyclic organopolysiloxane with general formula (II). Likewise, the compound with the formula

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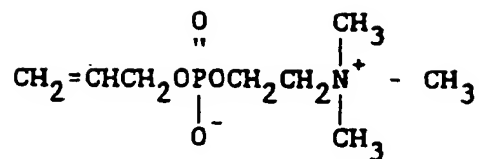
is a typical example of the cyclic dialkylsiloxane-alkylhydrogensiloxane copolymer starting material. Other examples are the above-mentioned polysiloxanes in which a portion of the methyl groups has been replaced by other alkyl groups.

45 Specific examples of formula (IV) compounds are as follows:

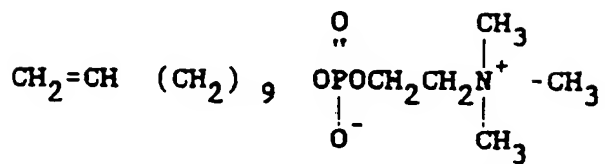
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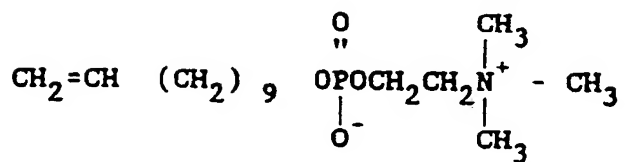
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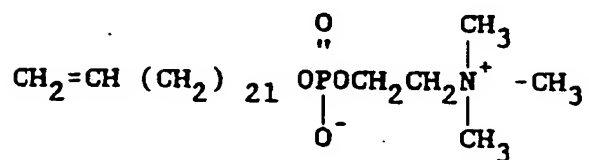
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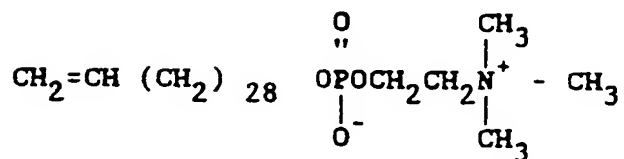
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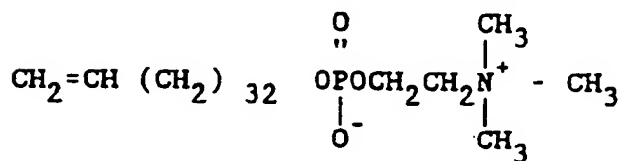
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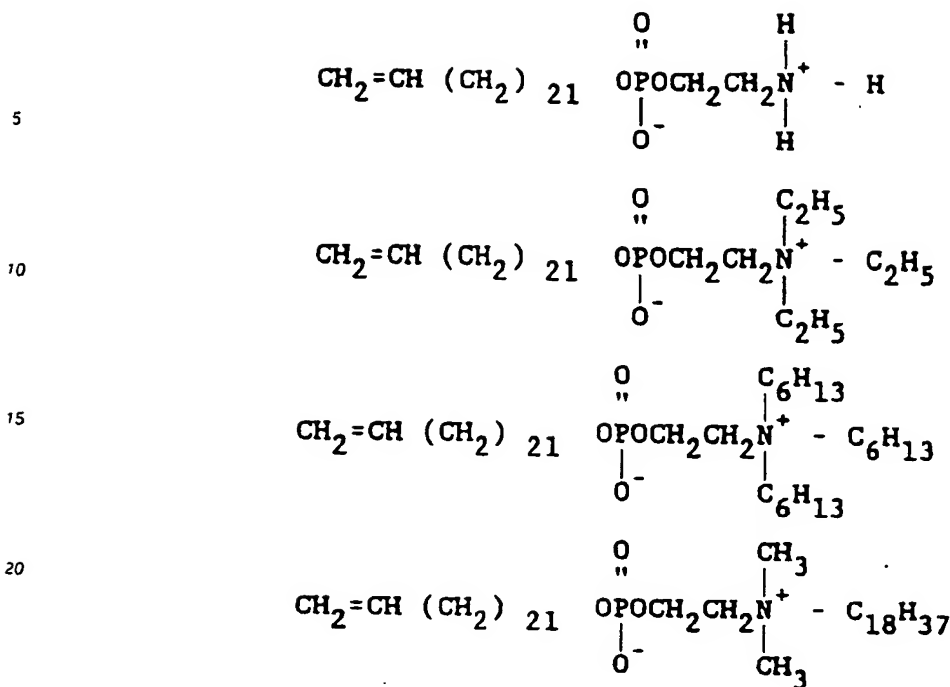
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Formula (IV) compounds can be synthesized, for example, by the condensation of an alcohol with the formula $\text{CH}_2=\text{CH}-(\text{CH}_2)_w-\text{OH}$ with 2-chloro-2-oxo-1,3,2-dioxaphospholane over a hydrochloric acid acceptor and by reacting the product with tertiary amine or ammonia.

A hydrosilylation catalyst is required to carry out the hydrosilylation reaction between the alkylhydrogenpolysiloxane and the formula (IV) compound.

Said hydrosilylation catalysts encompass compounds of platinum, ruthenium, rhodium, and palladium, for example, platinum dichloride, chloroplatinic acid, sodium chloroplatinate, platinum/olefin complex salts, platinum/beta-diketone complex salts, platinum/beta-diketoacid ester complex salts, chloroplatinic acid/1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex salts, microparticulate platinum, and finely divided platinum supported on alumina.

While the alkylhydrogenpolysiloxane/formula (IV) compound hydrosilylation reaction can be run by directly reacting both compounds, where possible they may be dissolved in a common solvent, a suitable amount of hydrosilylation catalyst is added to the solution, and this is then stirred at room temperature or with heating.

Said common solvents are exemplified by toluene, xylene, chloroform, and 1,1,1-trichloroethane. After completion of the reaction, the target compound is obtained by removing the hydrosilylation catalyst and distilling off the organic solvent. Alternatively, the reaction solution is poured into a large quantity of a poor solvent in order to reprecipitate the product, which is then filtered off.

The formula (III) organic group will be directly bonded to those silicon atoms in the starting alkylhydrogenpolysiloxane which had hydrosilyl groups.

Accordingly, formula (III) organic groups will be pendant on the molecular chain when the hydrosilyl groups in the alkylhydrogenpolysiloxane are pendant, and formula (III) organic groups will be present at the molecular chain terminals when the hydrosilyl groups are present at the molecular chain terminals.

The formula (III) organic groups will be present both pendant and at the molecular chain terminals when the hydrosilyl groups are present both pendant on the molecular chain and at the molecular chain terminals.

This invention's organopolysiloxanes are generally solids and occasionally liquids at room temperature. The presence of the formula (III) organic group generates hygroscopicity and hydrophilicity when its concentration is high.

Liquid crystallinity appears at large values of n in the formula (III) organic group.

The presence of the phospholipid-like formula (III) organic group also confers biocompatibility.

Furthermore, when 3 or more hydrosilyl groups are present in each molecule, an elastomer can be formed by self-crosslinking in the presence of a condensation catalyst. An elastomer can also be formed from mixtures of the compound having 2 or more hydrosilyl groups in the molecule with curing catalyst and

organopolysiloxane having two or three or more silanol or vinyl groups in each molecule.

The present invention's organopolysiloxane containing a phospholipid-like structure is useful in a wide range of applications, such as for liquid crystal displays, artificial visceral organs, ion-exchange membranes, humidity sensors, gas sensors, biosensors, etc.

5 The following examples illustrate several of the specific embodiments of the invention. The examples are presented to help those skilled in the art to better understand the extent and scope of the instant invention as defined in the claims in light of this application.

In the examples and reference examples, IR refers to the infrared absorption spectrum.

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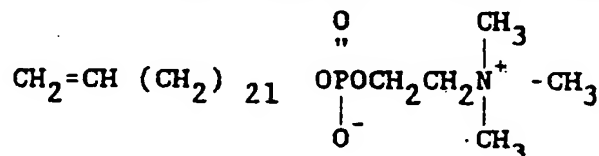
Reference Example i

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Synthesis of 22-tricosenyl

2-(trimethylammonio)ethyl phosphate

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Herein, 3.38 g 22-tricosenyl alcohol (0.010 mol) was dissolved in 150 mL dry tetrahydrofuran, 1.21 g triethylamine (0.012 mol) was added, and after cooling to -5 degrees Centigrade, 1.74 g 2-chloro-2-oxo-1,3,2-dioxaphospholane (0.012 mol) was added dropwise over 30 minutes with stirring.

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After the completion of addition, the reaction was continued at 5 to 10 degrees Centigrade with stirring for 2 hours, the precipitated triethylamine hydrochloride was then filtered off, and the filtrate was concentrated under reduced pressure to remove the tetrahydrofuran. The residual liquid was combined with 100 mL dimethylformamide and 2.95 g trimethylamine (0.050 mol), and this was placed in a pressure-resistant glass bottle, sealed, and then reacted at 75 degrees Centigrade for 36 hours with shaking.

The dimethylformamide was then distilled off in vacuo. The product, a viscous liquid, was dissolved in 5 mL methanol, which was then poured into a large volume of diethyl ether to obtain a white precipitate.

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The white precipitate was collected on a glass filter and then dried in vacuo to obtain a white powder.

This white powder was subjected to IR analysis, and the presence of the following was confirmed: methylene (2925 cm⁻¹, 2850 cm⁻¹, and 1450 cm⁻¹), vinyl (1620 cm⁻¹), P=O (1230 cm⁻¹), and (P=O)-CH₂- (1040 cm⁻¹ and 930 cm⁻¹).

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¹H-NMR examination of the white powder confirmed the presence of the following:

-CH₂- (δ = 1.3, 6 OH), C=C-CH₂ (δ = 1.9, 2H) N⁺-CH₃ (δ = 3.4, 9H), N⁺-CH₂ (δ = 3.8, 2H) O-CH₂ (δ = 4.0, 4H), H-C=C (δ = 4.9, 1H) H-C=C-H (δ = 5.6, 1H), =C-H (δ = 5.9, 1H)

This white powder was thus confirmed to be 22-tricosenyl 2-(trimethylammonio)ethyl phosphate.

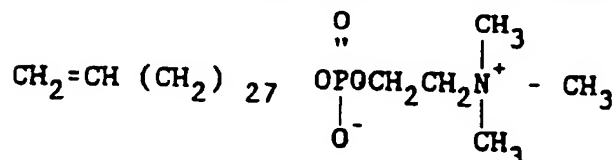
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Reference Example 2

**Synthesis of 28-nonacosenyl
2-(trimethylammonio)ethyl phosphate**



Herein, 4.22 g 28-nonacosenyl alcohol (0.010 mol) was dissolved in 150 mL dry tetrahydrofuran, 1.21 g triethylamine (0.012 mol) was added, and after cooling to -5 degrees Centigrade, 1.74 g 2-chloro-2-oxo-1,3,2-dioxaphospholane (0.012 mol) was added dropwise over 30 minutes with stirring.

After the completion of addition, the reaction was continued at 5 to 10 degrees Centigrade with stirring for 2 hours, the precipitated triethylamine hydrochloride was then filtered off, and the filtrate was concentrated under reduced pressure to remove the tetrahydrofuran. The residual liquid was combined with 100 mL dimethylformamide and 2.95 g trimethylamine (0.050 mol), and this was placed in a pressure-resistant glass bottle, sealed, and then reacted at 75 degrees Centigrade for 36 hours with shaking.

The dimethylformamide was then distilled off in vacuo. The product, a viscous liquid, was dissolved in 5 mL methanol, which was then poured into a large volume of diethyl ether to obtain a white precipitate.

The white precipitate was collected on a glass filter and then dried in vacuo to obtain a white powder.

This white powder was subjected to IR analysis, and the presence of the following was confirmed: methylene (2925 cm⁻¹, 2850 cm⁻¹, and 1450 cm⁻¹), vinyl (1620 cm⁻¹), P=O (1230 cm⁻¹), and (P=O)-CH₂- (1040 cm⁻¹ and 930 cm⁻¹).

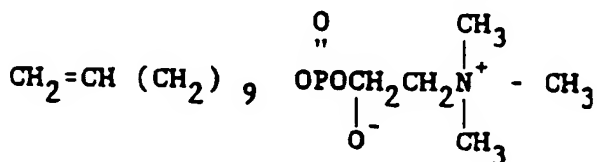
¹H-NMR examination of the white powder confirmed the presence of the following.

-CH₂- (δ = 1.3, 6 OH), C=C-CH₂ (δ = 1.9, 2H) N⁺-CH₃ (δ = 3.4, 9H), N⁺-CH₂ (δ = 3.8, 2H) O-CH₂ (δ = 4.0, 4H), H-C=C (δ = 4.9, 1H) H-C=C-H (δ = 5.6, 1H), =C-H (δ = 5.9, 1H)

This white powder was thus confirmed to be 28-nonacosenyl 2-(trimethylammonio)ethyl phosphate.

Reference Example 3

**Synthesis of 10-undecenyl
2-(trimethylammonio)ethyl phosphate**



Herein, 7.60 g 10-undecen-1-ol (0.0451 mol) was dissolved in 200 mL dry tetrahydrofuran, 6.85 g triethylamine (0.0670 mol) was added, and after cooling to -20 degrees Centigrade, 7.85 g 2-chloro-2-oxo-1,3,2-dioxaphospholane (0.0540 mol) was added dropwise over 30 minutes with stirring.

After the completion of addition, the reaction was continued at 5 degrees Centigrade with stirring for 2 hours, the precipitated triethylamine hydrochloride was then filtered off, and the filtrate was concentrated under reduced pressure to remove the tetrahydrofuran. The residual liquid was combined with 150 mL dimethylformamide and 5.00 g trimethylamine (0.0847 mol), and this was placed in a pressure-resistant glass bottle, sealed, and then reacted at 75 degrees Centigrade for 20 hours with shaking.

The dimethylformamide was then distilled off in vacuo. The product, a viscous liquid, was dissolved in 5

mL methanol, which was then poured into a large volume of diethyl ether to obtain a white precipitate.

The white precipitate was collected on a glass filter and then dried in vacuo to obtain a white powder.

This white powder was subjected to IR analysis, and the presence of the following was confirmed: methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1450 cm^{-1}), vinyl (1620 cm^{-1}), $\text{P}=\text{O}$ (1230 cm^{-1}), and $(\text{P}=\text{O})\text{-CH}_2\text{-}$ (1040 cm^{-1} and 930 cm^{-1}).

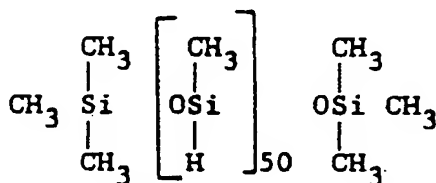
$^1\text{H-NMR}$ examination of the white powder confirmed the presence of the following.

$-\text{CH}_2-$ ($\delta = 1.3$, 6 OH), $\text{C}=\text{C}-\text{CH}_2$ ($\delta = 1.9$, OH) $\text{N}^+ - \text{CH}_3$ ($\delta = 3.4$, 9H), $\text{N}^+ - \text{CH}_2$ ($\delta = 3.8$, 2H) $\text{O}-\text{CH}_2$ ($\delta = 4.0$, 4H), $\text{H}-\text{C}=\text{C}$ ($\delta = 4.9$, 1H) $\text{H}-\text{C}=\text{C}-\text{H}$ ($\delta = 5.6$, 1H), $=\text{C}-\text{H}$ ($\delta = 5.9$, 1H)

This white powder was thus confirmed to be 10-undecenyl 2-(trimethylammonio)ethyl phosphate.

Example 1

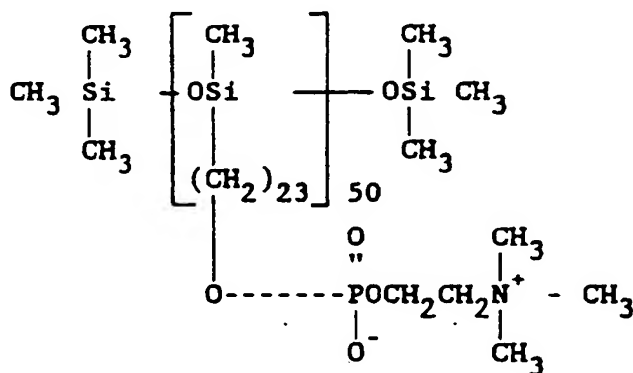
Herein, 0.0503 g ($0.159 \times 10^{-4}\text{ mol}$) methylhydrogenpolysiloxane with the formula



and 0.4000 g ($7.94 \times 10^{-4}\text{ mol}$) 22-tricosenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 1 were dissolved in 30 mL warm toluene. Chloroplatinic acid was also added to and dissolved in this toluene solution at the rate of 220 to 275 micromoles/L. The resulting solution was placed in a pressure-resistant glass bottle, which was sealed and immersed in a water bath at 80 degrees Centigrade for 24 hours in order to carry out a hydrosilylation reaction. Upon completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and dried.

The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670 cm^{-1}) and hydrosilyl (2240 cm^{-1}); presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), $\text{P}=\text{O}$ (1200 cm^{-1}), and $(\text{P}=\text{O})\text{-CH}_2\text{-}$ (1060 cm^{-1}).

The product was thus a polysiloxane with the formula

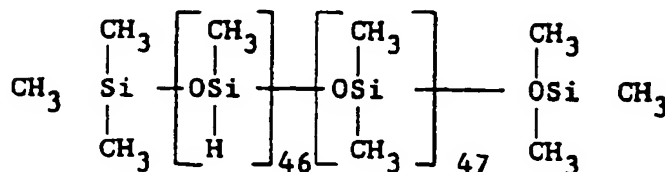


that is, a trimethylsiloxy-terminated methyl[(trimethylammonium)ethylphosphatidyltricosyl]polysiloxane.

When the product's thermal changes were examined under a polarizing microscope, it was found to be a nematic liquid crystal in the temperature interval of 25 to 195 degrees Centigrade.

Example 2

Herein, 0.111 g (0.173×10^{-4} mol) methylhydrogenpolysiloxane with the formula:

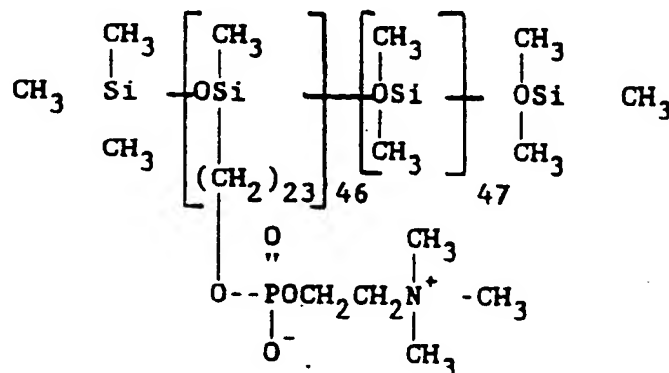


and 0.399 g (7.94×10^{-4} mol) 22-tricosenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 1 were dissolved in 30 mL warm toluene, and chloroplatinic acid was also added to and dissolved in the toluene solution at a ratio of 220 to 275 micromoles/L. The resulting solution was placed in a pressure-resistant glass bottle, which was then sealed and immersed in a water bath at 80 degrees Centigrade for 24 hours in order to carry out a hydrosilylation reaction.

After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and dried.

The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670 cm^{-1}) and hydrosilyl (2240 cm^{-1}); presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), $\text{P}=\text{O}$ (1200 cm^{-1}), and $(\text{P}=\text{O})-\text{CH}_2-$ (1060 cm^{-1}).

The product was thus a polysiloxane with the formula

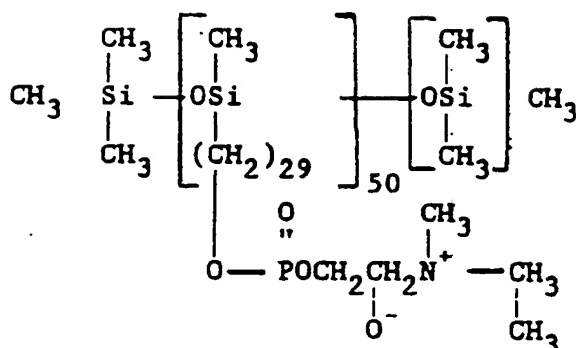


that is, a trimethylsiloxy-terminated methyl[(trimethylammonium)ethylphosphatidyltricosyl]siloxane-dimethylsiloxane copolymer. The product's thermal changes were examined under a polarizing microscope, and it was confirmed to be a nematic liquid crystal in the temperature interval of 83 to 185 degrees Centigrade.

Example 3

Herein, 0.0503 g (0.159×10^{-4} mol) methylhydrogenpolysiloxane as used in Example 1 and 0.466 g (7.94×10^{-4} mol) 28-nonacosenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 2 were dissolved in 30 mL warm toluene, and chloroplatinic acid was also added to and dissolved in the toluene solution at a ratio of 220 to 275 micromoles/L. The obtained solution was placed in a pressure-resistant glass bottle, which was sealed and immersed in a water bath at 80 degrees Centigrade for 24 hours in order to carry out a hydrosilylation reaction. After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was then filtered off and dried.

The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670 cm^{-1}) and hydrosilyl (2240 cm^{-1}); presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), $\text{P}=\text{O}$ (1200 cm^{-1}), and $(\text{P}=\text{O})-\text{CH}_2-$ (1060 cm^{-1}). The product was thus a polysiloxane with the formula:



that is, a trimethylsiloxy-terminated methyl[(trimethylammonium)ethylphosphatidyl]nonacosyl polysiloxane.

This product's thermal changes were examined under a polarizing microscope, and it was confirmed to be a nematic liquid crystal in the temperature interval of 20 to 209 degrees Centigrade.

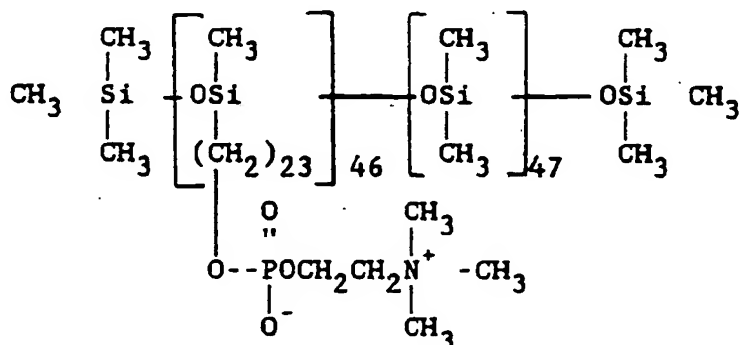
Example 4

Herein, 0.111 g (0.173×10^{-4} mol) methylhydrogenpolysiloxane as used in Example 2 and 0.466 g (7.94×10^{-4} mol) 28-nonacosenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 2 were dissolved in 30 mL warm toluene, and chloroplatinic acid was also added to and dissolved in this toluene solution at a ratio of 220 to 275 micromoles/L. The obtained solution was placed in a pressure-resistant glass bottle, which was then sealed and immersed in a water bath at 80 degrees Centigrade for 24 hours in order to carry out a hydrosilylation reaction.

After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and dried.

The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670 cm^{-1}) and hydrosilyl (2240 cm^{-1}); presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), P=O (1200 cm^{-1}), and (P=O)-CH₂- (1060 cm^{-1}).

The product was thus a polysiloxane with the formula:

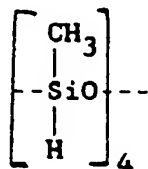


that is, a trimethylsiloxy-terminated methyl[(trimethylammonium)ethylphosphatidyl]nonacosyl - dimethylsiloxy copolymer.

The product's thermal changes were examined under a polarizing microscope, and it was found to be a nematic liquid crystal in the temperature interval of 75 to 198 degrees Centigrade.

Example 5

Herein, 0.0476 g (1.99×10^{-4} mol) methylhydrogenpolysiloxane with the formula:

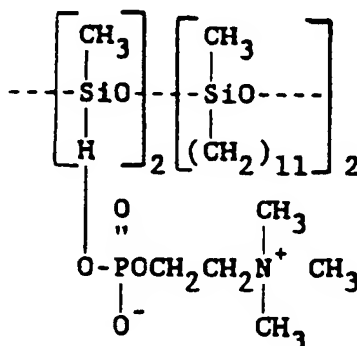


and 0.133 g (3.97×10^{-4} mol) 10-undecenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 3 were dissolved in 30 mL warm toluene, and chloroplatinic acid was also added to and dissolved in this toluene solution at a ratio of 220 to 275 micromoles/L. The obtained solution was placed in a pressure-resistant glass bottle, which was then sealed and immersed in a water bath for 20 hours at 75 degrees Centigrade in order to carry out the hydrosilylation reaction.

After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and dried.

The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670 cm^{-1}); hydrosilyl (2240 cm^{-1}) reduced by half; presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), $\text{P}=\text{O}$ (1200 cm^{-1}), and $(\text{P}=\text{O})\text{-CH}_2\text{-}$ (1060 cm^{-1}).

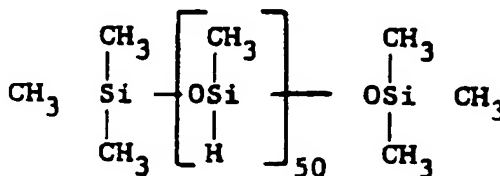
Dibutyltin dilaurate (1 wt% on product) was added to and mixed with a toluene solution of the product (1 wt% solids), resulting in condensation with the evolution of hydrogen gas. The product was thus a polysiloxane with the formula:



that is, a tetramethyldi[(trimethylammonium)ethyl]phosphatidylundecyl]dihydrogencyclo-tetrasiloxane.

Example 6

Herein 0.0617 g (0.195×10^{-4} mol) methylhydrogenpolysiloxane with the formula:

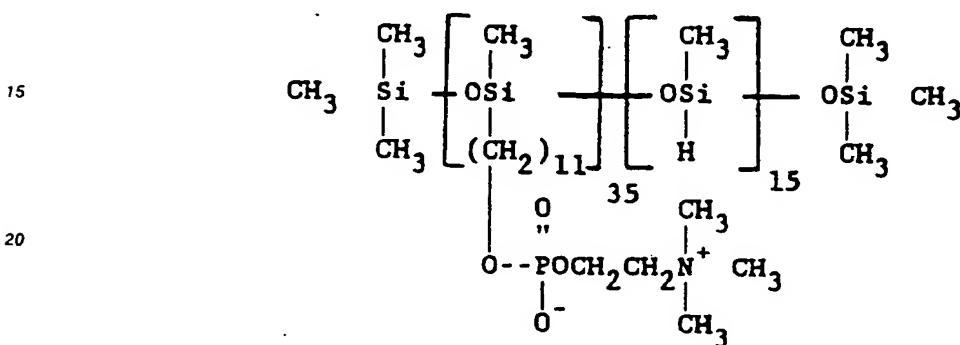


and 0.228 g (6.81×10^{-4} mol) 10-undecenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 3 were dissolved in 30 mL warm toluene, and chloroplatinic acid was added to and dissolved in this toluene solution at a ratio of 220 to 275 micromoles/L. The obtained solution was placed in a pressure-resistant

glass bottle, which was then sealed and immersed in a water bath at 75 degrees Centigrade for 60 hours in order to carry out the hydrosilylation reaction.

After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and dried.

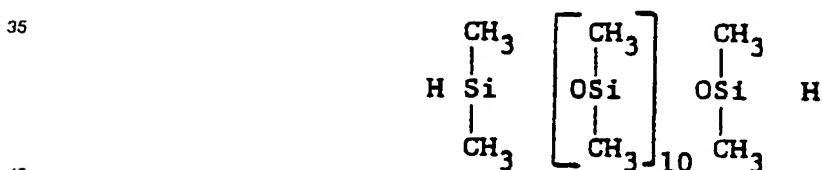
5 The product was a white, very slightly hygroscopic solid. IR analysis of this product gave the following results: disappearance of vinyl (1670 cm^{-1}); ca. 70% reduction in hydrosilyl (2240 cm^{-1}); presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), P=O (1200 cm^{-1}), and (P=O)-CH₂- (1060 cm^{-1}). When dibutyltin dilaurate (1 wt% on product) was added to and mixed with the product's toluene solution (1 wt% solids), condensation occurred with the evolution of hydrogen gas. The product was thus a polysiloxane with the formula:



25 that is, a trimethylsiloxy-terminated methyl[(trimethylammonium)ethylphosphatidylundecyl]siloxane-methyl-
hydrogensiloxane copolymer.

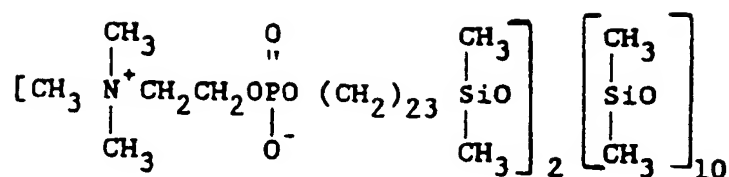
30 Example 7

Herein, 0.347 g (3.97×10^{-4} mol) methylhydrogenpolysiloxane with the formula:



and 0.400 g (7.94×10^{-4} mol) 22-tricosenyl 2-(trimethylammonio)ethyl phosphate from Reference Example 1 were dissolved in 30 mL warm toluene, and chloroplatinic acid was also added to and dissolved in this toluene solution at a ratio of 220 to 275 micromoles/L. The resulting solution was placed in a pressure-resistant glass bottle, which was then sealed and immersed in a water bath at 80 degrees Centigrade for 24 hours in order to carry out a hydrosilylation reaction. After completion of the reaction, the contents were removed and poured into a large excess of acetone for reprecipitation. The precipitate was filtered off and then dried. The product was a white, very slightly hygroscopic solid. IR analysis of this product provided the following results: disappearance of vinyl (1670 cm^{-1}) and hydrosilyl (2240 cm^{-1}); presence of methylene (2925 cm^{-1} , 2850 cm^{-1} , and 1460 cm^{-1}), P=O (1200 cm^{-1}), and (P=O)-CH₂- (1060 cm^{-1}).

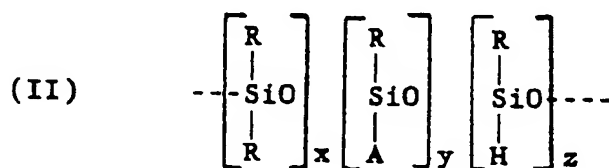
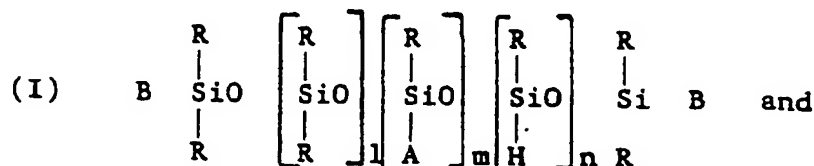
The product was thus a polysiloxane with the formula



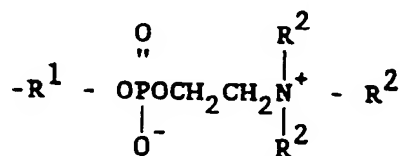
that is, a dimethyl[(trimethylammonium)ethylphosphatidyltricosyl]siloxyl-terminated dimethylpolysiloxane.

Claims

1. Organopolysiloxanes, containing a phospholipid-like structure, wherein the organopolysiloxanes are selected from siloxanes having the general formula

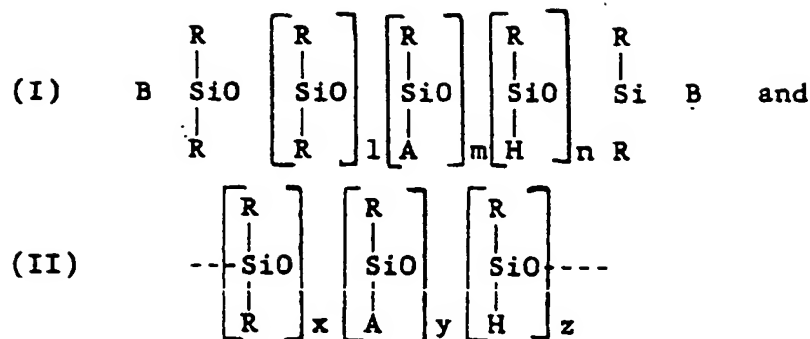


wherein each R is an alkyl radical; A is an organic group having the general formula

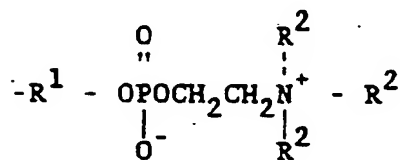


wherein R¹ is an alkylene group containing 3 to 50 carbon atoms and R² is selected from hydrogen atoms or an alkyl group containing 1 to 25 carbon atoms; B is selected from the group R, hydrogen atoms, or the group A; l, m, and n, each have a value of zero or an integer having a value of at least one, with the proviso that l + m + n is an integer having a value of 0 to 2,000; x and z are each zero or an integer of at least one; y is an integer of at least 1, with the proviso that z + y + x is an integer having a value of 3 to 20, and with the further proviso that there is at least one group containing A in each molecule.

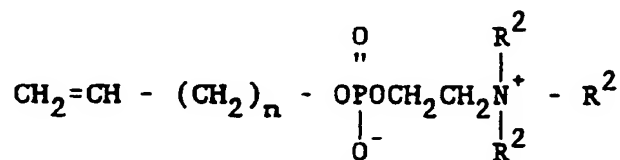
2. A process for the preparation of organopolysiloxanes, containing a phospholipid-like structure, wherein the organopolysiloxanes are selected from siloxanes having the general formula



wherein each R is an alkyl radical; A is an organic group having the general formula



wherein R¹ is an alkylene group containing 3 to 50 carbon atoms and R² is selected from hydrogen atoms or an alkyl group containing 1 to 25 carbon atoms; B is selected from the group R, hydrogen atoms, or the group A; l, m, and n, each have a value of zero or an integer having a value of at least one, with the proviso that l + m + n is an integer having a value of 0 to 2,000; x and z are each zero or an integer of at least one; y is an integer of at least 1, with the proviso that z + y + x is an integer having a value of 3 to 20, and with the further proviso that there is at least one group containing A in each molecule, the process comprising contacting a compound having the formula



with an organohydrogenpolysiloxane having at least one hydrogen bonded to silicon in each molecule, in the presence of a hydrosilylation catalyst, wherein n has a value of 1 to 48 and R² is defined above.

3. A process as claimed in claim 2, wherein the hydrosilylation catalyst is a platinum compound.

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